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(54) 1,5-ALKYLENE-3-ARYL HYDANTOIN DERIVATIVES

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a Japanese Body Corporate, of 5—2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, 100 Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hydantoin derivatives and, more particularly, to hydantoin derivatives having a substituted phenyl group on the nuclear nitrogen atom the in the 3-position which show valuable biological activity, particularly fungicidal and herbicidal activity.

The synthesis of certain 1,5-alkylene-3-aryl hydantoin derivatives, such as 1,5-trimethylene-3-phenyl hydantoin, 1,5-trimethylene-3-phenyl-2-thiohydantoin, 1,5-tetramethylene-3-phenyl hydantoin, 1,5-tetramethylene-3-(2',3' or 4'-chlorophenyl)-2-thiohydantoin, and 1,5-tetramethylene-3-(4'-tolyl)-2-thiohydantoin is known but their biological activities, especially herbicidal or fungicidal activity, have not previously been discovered [refer to E. Fischer: Chem. Ber. *34*, 1460 (1901), P. Edman: Acta Chem. Scand. *4*, 277 (1950), General Electric Co.,: French Patent 1,389,841 (1965), and B. Stanovnik: Croatica Chemica Acta *35*, 167 (1963)].

In general, it is believed that a biologically active compound causes some interaction with vital tissues to develop various actions. In the case of a compound having a herbicidal or weeding activity, it has been appreciated that absorption of the compound and its translocation in plants and the reaction at the site of action are the important factors, which are effected by the lipophilic-hydrophilic balance of the compound concerned.

It may be considered that the hydantoin derivatives of this invention have good lipophilic-hydrophilic balance based on the introduction of the alkylene chain attached to the 1- and 5-positions.

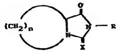
These characteristics play an important role in constituting to the herbicidal activity of these hydantoin derivatives.

In particular, the position of substituents on the phenyl ring attached to 3-position in the hydantoin ring may have a great influence on the herbicidal activity.

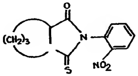
The hydantoin derivatives according to this invention can also be used as fungicides; e.g. 3,5-dihalogenophenyl compounds are very useful for controlling kidney bean gray mold, rice sheath and rice brown spot disease.

The terms "lower alkyl group" and "lower alkoxy group" are used herein to mean a C_1 to C_4 alkyl group and a C_1 to C_4 alkoxy group, respectively.

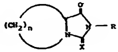
We are now aware that compounds of the formula



wherein X is sulphur, n is 3 or 4 and R is a phenyl group substituted by one or more halogen atoms, lower alkyl groups or lower alkoxy groups, and a compound of the formula



have been reported previously (see Offenlegungsschrift 1445797 and Journal of the American Chemical Society Vol LXXCIII 1956 pp 1255 to 1259) but not for use as herbicides or fungicides. Accordingly the present invention does not relate to these compounds as such but includes herbicidal and fungicidal compositions containing them and methods for their use as herbicides and as fungicides. Subject to this, the present invention provides a 1,5-Alkylene-3-substituted hydantoin having the general formula



Formula I

wherein n is 3 or 4, X is oxygen or sulphur, and R is a phenyl group having at least one substituent which is a halogen atom, a lower alkyl group, a lower alkoxy group, a nitro group, a haloalkyl group or a halogenobenzyloxy group, or a naphthyl group, provided that when n is 4 and X is sulphur, then R is not a monochlorophenyl group or a p-tolyl group.

The 1,5-alkylene-3-substituted hydantoin derivative of Formula I may preferably be one in which n is 3, X is oxygen or sulphur and R is a phenyl group having at least one substituent which is a halogen atom, a lower alkyl group, a lower alkoxy group or a halogenobenzyloxy group.

Other preferred compounds of Formula I are those in which n is 4, X is oxygen and R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group or halogenobenzyloxy group.

Other preferred compounds of Formula I are those in which n is 4, X is sulphur and R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group or a halogenobenzyloxy group.

Of these, particularly preferred are those in which R is a 4-bromophenyl, 4-iodophenyl, 4-(4'-chlorobenzyloxy)phenyl, 3-methyl-4-chlorophenyl, 3-methyl-4-bromophenyl, or 3,4-dichlorophenyl group.

Other preferred compounds of Formula I are those in which R is a phenyl group having at least one halogen atom at the 4-position of the benzene ring.

Other particularly preferred compounds of Formula I are those in which R is a 3,5-dichlorophenyl group.

The compounds of Formula I may be those in which X is oxygen and R is a mono or disubstituted phenyl group, the substituents independently being a halogen atom, a lower alkyl group, a lower alkoxy group, a haloalkyl group, a nitro group or a halogenobenzyloxy group.

The compounds of Formula I may be those in which X is sulphur, and R is phenyl having one or two substituents which are independently, halogen, lower alkyl, lower alkoxy, haloalkyl, nitro or chlorobenzyloxy.

The invention includes herbicidal and fungicidal compositions containing a compound of the invention as an active ingredient together with a carrier. In

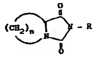
particular, the invention includes herbicidal compositions containing compounds of the invention in which R is a 4-halophenyl, 3-methyl-4-halophenyl, 4-(4'-halobenzyloxy) phenyl, or 3,4-dichlorophenyl group, and more particularly in which R is a 4-bromophenyl, 4-iodophenyl, 4-(4'-chlorobenzyloxy) phenyl, 3-methyl-4-chlorophenyl, 3-methyl-4-bromophenyl or 3,4-dichlorophenyl group.

The herbicidal composition may contain a compound of Formula 1 in which R is phenyl substituted by nitro, halogen, lower alkyl, lower alkoxy, trifluoromethyl, or chlorobenzyloxy, or is naphthyl.

The present invention further provides a method of killing fungus or of preventing or controlling the growth of fungus which method comprises applying a compound of the invention or a fungicidal composition of the invention to a susceptible fungus or an area on which the growth of fungus is to be prevented.

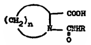
The present invention also provides methods for making the compounds of the invention which are:

a) A method for producing a 1,5-alkylene-3-substituted hydantoin derivative represented by the general formula



Formula II

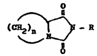
wherein n is 3 or 4, R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group, nitro group, haloalkyl group or halogenobenzyloxy group, which method comprises cyclizing an N-(N'-substituted carbamyl) imino acid represented by the general formula



Formula III

wherein n and R are as defined for Formula II.

b) A method for producing a 1,5-alkylene-3-substituted hydantoin derivative represented by the general formula



Formula II

wherein n is 3 or 4, R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group, nitro group, haloalkyl group or halogenobenzyloxy group which method comprises reacting an imino acid represented by the general formula

Formula IV

with an aryl isocyanate acid represented by the general formula

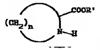
OCN—R

wherein R and n are as defined for Formula II.

c) A method for producing a 1,5-alkylene-3-substituted hydantoin derivative of the invention wherein x is sulphur, which method comprises reacting an imino acid represented by general formula

Formula IV

or an imino acid ester of the general formula



Formula VI

wherein R' is a lower alkyl group, and n is 3 or 4 with an aryl isothiocyanate represented by general formula

SCN—R

wherein R is as defined for Formula I above.

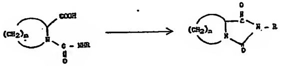
The present invention includes a method of controlling plant or fungal growth or of killing plants or fungus by applying compositions or compounds of the invention to plants or areas to be protected.

The compounds according to this invention can be prepared by various routes. Where X in general formula I is oxygen, then the compound may be prepared by Route A or B.

On the other hand, where, in general formula I, X is sulfur, the compound may be prepared by Route C or D.

Route A.

The 1,5-alkylene-3-aryl hydantoin compounds according to this invention may be prepared by cyclizing a N-(N'-substituted carbamyl) imino acid represented by general formula III



(III) (II)

wherein R and n have the same meaning as in formula I.

The compound represented by general formula III which is a starting material of this process can be prepared by reacting an imino acid (e.g. proline or pipecolinic acid), in water in the presence of an alkali, such as sodium hydroxide, potassium hydroxide, barium hydroxide or calcium hydroxide, with an aryl isocyanate in an appropriate solvent, such as benzene, chlorobenzene, ether or DMF at 0—50°C for 0.5—6 hours. The resulting N-(N'-substituted carbamyl) imino acid III may be purified, if desired, by recrystallization from an appropriate solvent such as acetone.

One embodiment of the production of N-(N'-substituted carbamyl) imino acid will be explained by way of the following Reference Example.

Reference Example.

To a solution of 1.73 g (0.015 mole) of proline and 0.6 g (0.015 mole) of sodium hydroxide in 25 ml of water was added 2.81 g (0.015 mole) of m-trifluoromethylphenyl isocyanate in 20 ml of chlorobenzene. After stirring for 2 hours at room temperature, the reaction mixture was extracted with ether. To the aqueous phase was added concentrated hydrochloric acid to pH 4, then the resulting bulk was collected by filtration and washed with water. After recrystallization from acetone-water, 4.0 g of N-[N'(m-trifluoromethylphenyl) carbamyl] proline having a melting point of 178—180°C was obtained.

The elementary analysis as $C_{13}H_{13}O_3N_2F_3$ was:

	C%	H%	N%
Calcd.	51.66	4.33	9.27
Found	51.37	4.12	9.22

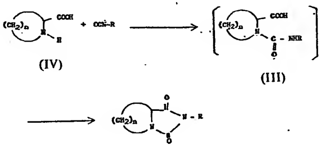
In carrying out the procedure of Route A, the compound III is suitably cyclized in the presence of acid catalyst such as hydrochloric acid or sulfuric acid in an appropriate aqueous solvent such as water, dioxane-water, DMF-water or THF-water at 50—150°C for 0.5—6 hours.

The cyclized product can be isolated by filtration of the crystals produced by cooling the reaction mixture to room temperature. If desired, the product may be

purified, for example by recrystallization from an appropriate solvent such as ethanol, 2-propanol or acetone or by column chromatography or by a combination thereof.

Route B.

In this route, an imino acid e.g. proline or pipecolinic acid, represented by general formula IV is employed as a starting material and is reacted with an aryl isocyanate. This is a conventional method which has merit that the intermediate compound, N-(N'-substituted carbamyl) imino acid III, is not necessarily isolated.



(IV) (III) (II)

wherein R and n have the same meanings defined in formula I.

The N-carbamylation reaction is carried out as described in the Reference Example in *Route A*, but a larger amount of acid is added to the extracted aqueous phase to keep the pH at 2.

The cyclization reaction is successively performed by heating the above obtained acidic mixture under the same conditions as are described in *Route A*.

Route C.

In this route, an imino acid IV is reacted with an aryl isothiocyanate to give a 1,5-alkylene-3-aryl-2-thiohydantoin V in accordance with the following scheme:

(IV) (V)

wherein R and n have the same meanings defined in formula 1.

The 2-thiohydantoin formation reaction according to this route is suitably performed by heating a mixture of an imino acid IV, an aryl isothiocyanate, and a solvent under reflux condition for 0.15—2 hours. Examples of solvents which may be employed in this route include, preferably, an alcohol, such as ethanol, 1-propanol, 2-propanol or methanol; and DMF, THF, benzene or toluene.

The reaction product is obtained by filtration of precipitated crystals which is resulted by cooling the reaction mixture or evaporation of the solvent.

Purification is accomplished, if desired, by recrystallization from an appropriate solvent such as methanol, ethanol, ethyl acetate, acetone or water or by column chromatography.

Route D.

In this route, an imino acid ester VI is reacted with an aryl iosthiocyanate to give a 1,5-alkylene-3-aryl-2-thiohydantoin according to the scheme:

(VI) (V)

wherein R and n have the same meanings defined in formula I, and R' is a lower alkyl group, such as methyl or ethyl.

The formation of 2-thiohydantoin derivatives according to this route is suitably performed by heating a mixture of an imino acid ester, an aryl isothiocyanate, and a solvent under reflux conditions for 0.15—3 hours.

Examples of solvents which may be employed in this route include, preferably, an alcohol, such as ethanol, 1-propanol, 2-propanol or methanol; and DMF, THF, benzene or toluene.

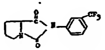
The reaction product is obtained by filtration of precipitated crystals which is resulted by cooling the reaction mixture or evaporation of the solvent.

Purification is accomplished, if desired, by recrystallization from an appropriate solvent such as methanol, ethanol, ethyl acetate, acetone or water by column chromatography or by a combination thereof.

The following Examples illustrate these methods of preparing compounds of the present invention. It should be understood that this invention is not limited by these Examples. The letter shown in parenthesis after the Example number shows the Route employed.

Preparative Example 1 (A).

A mixture of 3.02 g (0.01 mole) of N-(3-trifluoromethyl)-carbamoyl proline (mp. 178—80°C), 40 ml of 2N hydrochloric acid, and 10 ml of dioxane was heated under reflux condition for 2 hours with stirring. After cooling to room temperature, the resulting crystals were collected by filtration, washed with water, and recrystallized from acetone-water to obtained 2.62 g (the yield being 92.2%) of 3-(3'-trifluoromethyl-phenyl) 1,5-trimethylenehydantoin, having a melting point of 133—6°C.

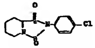


The elementary analysis as $C_{13}H_{11}O_2N_2F_3$ was:

	C%	H%	N%
Calcd.	54.93	3.90	9.86
Found	55.05	3.86	9.63

Preparative Example 2 (B).

To a solution of 1.94 g (0.015 mole) of pipecolinic acid and 0.6 g (0.015 mole) of sodium hydroxide in 25 ml of water was added 2.30 g (0.015 mole) of p-chlorophenyl iso-cyanate in 20 ml of chlorobenzene. After stirring for 4 hours at room temperature, the reaction mixture was extracted with ether. Then concentrated hydrochloric acid was added to aqueous phase to pH 2, and the acidic mixture was heated under reflux condition for one hour with stirring. After cooling to the room temperature, the resulting crystals were collected by filtration, washed with water, and recrystallized from 2-propanol to obtain 3.22 g (the yield being 81.1%) of 3-(p-chlorophenyl)-1,5-tetramethylenehydantoin, the melting point being 157—8°C.



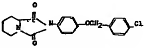
The elementary analysis as $C_{13}H_{13}O_2N_2Cl$ was:

	C%	H%	N%	Cl%
Calcd.	58.98	4.95	10.58	13.40
Found	59.11	4.96	10.42	13.46

Preparative Example 3 (B)

To a solution of 1.29 g (0.01 mole) of pipecolinic acid and 0.4 g (0.01 mole) of sodium hydroxide in 20 ml of water was added 2.60 g (0.01 mole) of 4-(p-chlorobenzyloxy) phenyl isocyanate in 10 ml of DMF. After stirring for 4 hours, to the reaction mixture was added concentrated hydrochloric acid to pH 2 and the mixture was heated under reflux condition for 2 hours with stirring. After cooling

to room temperature, the resulting crystals were collected by filtration, washed with water, and recrystallized from DMF-ethanol to obtain 2.93 g (the yield being 79.0%) of 3-[4'-(4"-chlorobenzyloxy)-phenyl]-1,5-tetramethylenehydantoin, the melting point being 52—3°C.



The elementary analysis as $C_{20}H_{19}O_3N_2Cl$ was:

	C%	H%	N%	Cl%
Calcd.	64.78	5.17	7.56	9.56
Found	64.72	5.01	7.43	9.55

By the procedures described in Examples 1—3, the compounds listed in Table 1 were also prepared.

TABLE 1

No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	X	Example No.	Yield (%)
1	1,5-trimethyl-3-(3′-trifluoromethylphenyl)-hydantoin	133 – 6	Calcd. 54.93 Found 55.07	3.90 3.88	9.86 9.71		1	92.2
2	1,5-trimethylene-3-(4′-methylphenyl) hydantoin	158 – 60	67.81 67.58	6.13 5.96	12.17 12.11		2	75.3
3	1,5-trimethylene-3-(4′-methoxyphenyl) hydantoin	124 – 5	63.40 63.61	5.73 5.77	11.38 11.35		2	76.0
4	1,5-trimethylene-3-(4′-ethoxyphenyl) hydantoin	121 – 2	64.60 64.51	6.20 6.18	10.76 10.70		2	71.2
5	1,5-trimethylene-3-(4′-fluorophenyl) hydantoin	142.5–4.5	61.53 61.61	4.73 4.88	11.96 11.69		2	75.5
6	1,5-trimethylene-3-(4′-chlorophenyl) hydantoin	138.5–9.5	57.49 57.41	4.42 4.39	11.18 11.09	X=Cl 14.14 14.28	1	90.0
7	1,5-trimethylene-3-(4′-bromophenyl) hydantoin	174 – 6	48.83 48.61	3.76 3.70	9.49 9.36	X=Br 27.08 27.14	2	78.8
8	1,5-trimethylene-3-(3′,4′-dichlorophenyl) hydantoin	142 – 3	50.55 50.51	3.54 3.50	9.83 9.60	X=Cl 24.87 24.61	2	77.4

TABLE 1 (cont.)

No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	X	Example No.	Yield (%)
9	1,5-tetramethylene-3-(3'-fluorophenyl) hydantoin	117 – 8.5	62.89 62.75	5.28 5.26	11.29 11.35		2	74.8
10	1,5-tetramethylene-3-(3'-chlorophenyl) hydantoin	132 – 3	58.98 58.90	4.95 4.86	10.58 10.32	X=Cl 13.40 13.51	2	70.2
11	1,5-tetramethylene-3-(3'-bromophenyl) hydantoin	138 – 9	50.50 50.54	4.24 4.02	9.06 9.13	X=Br 25.85 25.79	2	73.8
12	1,5-tetramethylene-3-(3'-methylphenyl) hydantoin	126 – 7	68.83 68.91	6.60 6.66	11.47 11.41		2	67.3
13	1,5-tetramethylene-3-(3'-trifluoromethylphenyl)-hydantoin	158 – 9.5	56.37 56.51	4.39 4.44	9.39 9.28		1	88.9
14	1,5-tetramethylene-3-(3'-nitrophenyl) hydantoin	164 – 5	56.72 56.77	4.76 4.82	15.27 15.14		2	81.2
15	1,5-tetramethylene-3-(4'-methylphenyl) hydantoin	184.5–6	68.83 68.95	6.60 6.63	11.47 11.38		2	79.6
16	1,5-tetramethylene-3-(4'-methoxyphenyl) hydantoin	136.5–8	64.60 64.59	6.20 6.28	10.76 10.72		2	78.7

TABLE 1 (cont.)

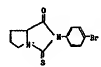
No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	X	Example No.	Yield (%)
17	1,5-tetramethylene-3-(4'-ethoxyphenyl) hydantoin	129 – 31	65.67 65.53	6.61 6.78	10.21 10.25		2	75.5
18	1,5-tetramethylene-3-(4'-fluorophenyl) hydantoin	141.5–3	62.89 63.60	5.28 5.38	11.29 11.16		2	80.0
19	1,5-tetramethylene-3-(4'-chlorophenyl) hydantoin	157 – 8	58.98 59.11	4.95 4.96	10.58 10.42	X=Cl 13.40 13.46	2	81.1
20	1,5-tetramethylene-3-(4'-bromophenyl) hydantoin	175 – 7	50.50 50.28	4.24 4.16	9.06 8.87	X=Br 25.85 25.99	2	82.1
21	1,5-tetramethylene-3-(4'-iodophenyl) hydantoin	206 – 7	43.84 43.99	3.68 3.69	7.87 7.68		2	73.3
22	1,5-tetramethylene-3-(4'-nitrophenyl) hydantoin	190 – 1	56.72 56.68	4.76 4.81	15.27 15.23		2	76.5
23	1,5-tetramethylene-3-(3',4'-dichlorophenyl) hydantoin	187 – 90	52.19 51.92	4.04 3.88	9.37 9.18	X=Cl 23.71 23.91	2	81.5
24	1,5-tetramethylene-3-(3',4'-dimethylphenyl) hydantoin	155 – 6	69.74 69.68	7.02 7.11	10.85 10.72		2	69.8

TABLE 1 (cont.)

No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	X	Example No.	Yield (%)
25	1,5-tetramethylene-3-(3′-methyl-4′-chlorophenyl)-hydantoin	172 – 3	60.32 60.29	5.42 5.41	10.05 10.01	X=Cl 12.72 12.81	2	79.4
26	1,5-tetramethylene-3-(3-methyl-4′-bromophenyl)-hydantoin	186.5–8	52.02 51.89	4.68 4.68	8.67 8.51	X=Br 24.73 24.91	2	77.5
27	1,5-tetramethylene-3-[4′-(4′′-chlorobenzyloxy) phenyl]-hydantoin	152 – 3	64.78 64.72	5.17 5.01	7.56 7.43	X=Cl 9.56 9.55	3	79.0
28	1,5-trimethylene-3-(3′,5′-dichlorophenyl) hydantoin	169 – 71	50.55 50.43	3.54 3.47	9.83 9.95	X=Cl 24.87 24.78	2	66.0
29	1,5-tetramethylene-3-(3′,5′-dichlorophenyl) hydantoin	97 – 9	52.19 52.28	4.04 4.19	9.37 9.40	X=Cl 23.71 23.88	2	74.0

Preparative Example 4 (C).

A mixture of 1.15 g (0.01 mole) of proline, 2.14 g (0.01 mole) of p-bromophenyl isothiocyanate, and 15 ml of ethanol was heated under reflux condition for one hour. After cooling, the resulting crystals was collected by filtration and recrystallized from ethyl acetate-ethanol to obtain 2.60 g (the yield being 83.6%) of 3-(4′-bromophenyl)-1,5-trimethylene-2-thiohydantoin, the melting point being 159.5—61°C.

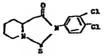


The elementary analysis as $C_{12}H_{11}ON_2SBr$ was:

	C%	H%	N%	S%	Br%
Calcd.	46.31	3.56	9.00	10.30	25.68
Found	46.08	3.29	8.78	10.29	25.59

Preparative Example 5 (C).

A mixture of 1.29 g (0.01 mole) of pipecolinic acid, 2.04 g (0.01 mole) of 3,4-dichlorophenyl isothiocyanate, and 15 ml of ethanol was heated under reflux condition for 20 minutes. After cooling, the resulting crystals were collected by filtration and recrystallized from DMF-ethanol to obtain 2.78 g (the yield being 88.3%) of 3-(3',4'-dichlorophenyl)-1,5-tetramethylene-2-thiohydantoin, the melting point being 219—22°C.

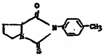


The elementary analysis as $C_{13}H_{12}ON_2SCl_2$ was:

	C%	H%	N%	S%	Cl%
Calcd.	49.53	3.84	8.89	10.17	22.50
Found	49.19	3.76	8.78	10.06	22.76

Preparative Example 6 (D).

A mixture of 1.43 g (0.01 mole) of 2-ethoxycarbonyl-pyrrolidine, 1.49 g (0.01 mole) of p-tolyl isothiocyanate, and 25 ml of ethanol was heated under reflux condition for two hours. After cooling, the resulting crystals were collected by filtration and recrystallized from ethanol to obtain 1.52 g (the yield being 61.8%) of 2-thio-3-(4'-tolyl)-1,5-trimethylenehydantoin, the melting point being 213—4.5°C.



The elementary analysis as $C_{13}H_{14}ON_2S$ was:

	C%	H%	N%	S%
Calcd.	63.38	5.27	11.37	13.02
Found	63.26	5.59	11.36	13.28

By the procedures described in Examples 4—6, the compounds listed in Table 2 were also prepared.

TABLE 2

No.	Compound	Melting point (°C)	Elementary analysis (%)					Example No.	Yield (%)
			C	H	N	S	X		
30	1,5-trimethylene-3-(3'-trifluoromethylphenyl)-2-thiohydantoin	125 – 7	51.99 51.76	3.69 3.61	9.33 9.25	10.68 10.66		4	74.5
31	1,5-trimethylene-3-(4'-methylphenyl)-2-thiohydantoin	213 – 4.5	63.38 63.39	5.73 5.71	11.37 11.29	13.02 13.10		6	61.8
32	1,5-trimethylene-3-(4'-methoxyphenyl)-2-thiohydantoin	181 – 3	59.52 59.50	5.38 5.33	10.68 10.75	12.22 12.35		4	77.6
33	1,5-trimethylene-3-(4'-chlorophenyl)-2-thiohydantoin	164 – 6.5	54.03 53.89	4.16 4.27	10.50 10.27	12.02 11.96	X=Cl 13.29 13.48	4	82.0
34	1,5-trimethylene-3-(4'-bromophenyl)-2-thiohydantoin	159.5–61	46.31 46.08	3.56 3.29	9.00 8.78	10.30 10.29	X=Br 25.68 25.59	4	83.6
35	1,5-trimethylene-3-(4'-nitrophenyl)-2-thiohydantoin	168.5–70	51.97 52.11	4.00 4.04	15.16 15.00	11.56 11.43		4	87.2
36	1,5-trimethylene-3-(3',4'-dichlorophenyl)-2-thiohydantoin	144.5–6	47.85 47.95	3.35 3.48	9.30 9.29	10.65 10.88	X=Cl 23.54 23.66	4	82.4
37	1,5-trimethylene-3-[4'-(4''-chlorobenzyloxy) phenyl]-2-thiohydantoin	187 – 8	61.20 61.22	4.60 4.60	7.51 7.48	8.60 8.59	X=Cl 9.51 9.28	4	84.3

TABLE 2 (cont.)

No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	S	X	Example No.	Yield (%)
38	1,5-tetramethylene-3-(2′-methylphenyl)-2-thiohydantoin	151.5–3	64.58 64.48	6.19 6.08	10.76 11.02	12.32 12.18		5	79.6
39	1,5-tetramethylene-3-(3′-methylphenyl)-2-thiohydantoin	147 – 8.5	64.58 64.66	6.19 6.23	10.76 10.61	12.32 12.33		5	80.6
40	1,5-tetramethylene-3-(3′-fluorophenyl)-2-thiohydantoin	140	59.07 59.25	4.96 5.03	10.60 10.48	12.13 12.22		5	76.8
41	1,5-tetramethylene-3-(3′-bromophenyl)-2-thiohydantoin	168.5–70	48.01 48.18	4.03 4.19	8.61 8.75	9.86 10.02	X=Br 24.57 24.68	5	80.0
42	1,5-tetramethylene-3-(3′-trifluoromethylphenyl)-2-thiohydantoin	172.5–4	53.49 53.41	4.17 4.08	8.91 8.99	10.20 10.12		5	82.5
43	1,5-tetramethylene-3-(4′-n-butylphenyl)-2-thiohydantoin	101.5–2	67.51 67.50	7.33 7.28	9.26 9.18	10.60 10.66		5	77.4
44	1,5-tetramethylene-3-(4′-methoxyphenyl)-2-thiohydantoin	138 – 40	60.84 61.06	5.84 6.12	10.14 10.01	11.60 11.76		5	81.1
45	1,5-tetramethylene-3-(4′-ethoxyphenyl)-2-thiohydantoin	161.5–2.5	62.04 62.28	6.25 6.33	9.65 9.81	11.04 11.03		5	76.9

TABLE 2 (cont.)

No.	Compound	Melting point (°C)	Elementary analysis (%) C	H	N	S	X	Example No.	Yield (%)
46	1,5-tetramethylene-3-(4′-fluorophenyl)-2-thiohydantoin	136 – 7	59.07 58.95	4.96 4.88	10.60 10.49	12.13 12.30		5	83.5
47	1,5-tetramethylene-3-(4′-bromophenyl)-2-thiohydantoin	180 – 2	48.01 47.86	4.03 4.01	8.61 8.43	9.86 9.81	X=Br 24.57 24.69	5	85.5
48	1,5-tetramethylene-3-(4′-iodophenyl)-2-thiohydantoin	210 – 2	41.94 41.64	3.52 3.28	7.53 7.41	8.61 8.56	X=I 34.10 34.36	5	82.7
49	1,5-tetramethylene-3-(4′-nitrophenyl)-2-thiohydantoin	188 – 91	53.59 53.81	4.50 4.72	14.43 14.69	11.01 10.84		5	87.2
50.	1,5-tetramethylene-3-(3′,4′-dichlorophenyl)-2-thiohydantoin	219 – 22	49.53 49.19	3.84 3.76	8.89 8.78	10.17 10.06	X=Cl 22.50 22.76	5	88.3
51	1,5-tetramethylene-3-(3′,4′-dimethylphenyl)-2-thiohydantoin	159 – 61	65.66 65.47	6.61 6.55	10.21 10.30	11.69 11.83		5	81.4
52	1,5-tetramethylene-3-(3′-methyl-4′-chlorophenyl)-2-thiohydantoin	195 – 8	57.04 57.15	5.13 5.28	9.50 9.75	10.88 10.68	X=Cl 12.03 12.15	5	88.7
53	1,5-tetramethylene-3-(3′-methyl-4′-bromophenyl)-2-thiohydantoin	215 – 6	49.56 49.69	4.46 4.60	8.26 8.08	9.45 9.58	X=Br 23.56 23.38	5	90.0

TABLE 2 (cont.)

No.	Compound	Melting point (°C)	Elementary analysis (%)					Example No.	Yield (%)
			C	H	N	S	X		
54	1,5-tetramethylene-3-[4'-(4''-chlorobenzyloxy) phenyl]-2-thiohydantoin	190 – 1	62.09 61.98	4.95 4.99	7.24 7.26	8.29 8.31	X=Cl 9.17 9.08	5	87.5
55	1,5-tetramethylene-3-(1'-naphthyl)-2-thiohydantoin	176 – 8	68.89 68.91	5.44 5.58	9.45 9.27	10.82 10.88		5	80.7
56	1,5-trimethylene-3-(3',5'-dichlorophenyl)-2-thiohydantoin	174 – 6	47.85 47.71	3.35 3.29	9.30 9.27	10.65 10.72	X=Cl 23.54 23.61	4	83.6
57	1,5-tetramethylene-3-(3',5'-dichlorophenyl)-2-thiohydantoin	184 – 6	49.53 49.54	3.84 3.76	8.89 8.72	10.17 10.11	X=Cl 22.50 22.59	5	88.5

These hydantoin derivatives have valuable biological activities, especially herbicidal or fungicidal activities. By the more detailed results, the sort and the position of substituents on the phenyl ring attached at the 3-position in the hydantoin ring may give a great influence on the biological activity which was brought about by the group dipole moment. So among these compounds, the compounds which have halogen, lower alkyl, lower alkoxyl or halogenobenzyloxy group at the 4-position of the phenyl group give excellent herbicidal activities. 3,4-Dihalogenophenyl compounds and 3-alkyl-4-halogenophenyl compounds show also strong herbicidal activities.

For example, among the compounds listed in Tables 1 and 2, the following compounds are most preferable as active ingredients of herbicides.

1,5-trimethylene-3-(4'-chlorophenyl) hydantoin,
1,5-trimethylene-3-(4'-bromophenyl) hydantoin,
1,5-trimethylene-3-(3',4'-dichlorophenyl) hydantoin,
1,5-tetramethylene-3-(4'-chlorophenyl) hydantoin,
1,5-tetramethylene-3-(4'-bromophenyl) hydantoin,
1,5-tetramethylene-3-(4'-iodophenyl) hydantoin,

1,5-tetramethylene-3-(3',4'-dichlorophenyl) hydantoin,
1,5-tetramethylene-3-[4'-(4"-chlorobenzyloxy) phenyl] hydantoin,
1,5-tetramethylene-3-(3'-methyl,4'-chlorophenyl) hydantoin,
1,5-tetramethylene-3-(3'-methyl,4'-bromophenyl) hydantoin,
1,5-tetramethylene-3-(4'-bromophenyl)-2-thiohydantoin,
1,5-tetramethylene-3-(4'-iodophenyl)-2-thiohydantoin,
1,5-trimethylene-3-(4'-chlorophenyl)-2-thiohydantoin,
1,5-trimethylene-3(4'-bromophenyl)-2-thiohydantoin,
1,5-trimethylene-3-(3',4'-dichlorophenyl)-2-thiohydantoin,
1,5-tetramethylene-3-(3'-methyl-4'-chlorophenyl)-2-thiohydantoin,
1,5-tetramethylene-3-(3'-methyl-4'-bromophenyl)-2-thiohydantoin,
1,5-tetramethylene-3-[4'-(4"-chlorobenzyloxy)phenyl]-2-thiohydantoin,
1,5-tetramethylene-3-(3',4'-dichlorophenyl)-2-thiohydantoin.

Herbicidal compositions containing these specifically identified hydantoin compounds of this invention possesses unique applicability to soil treatment and foliar treatment, and excellent herbicidal activity against grasses such as *Digitaria asscendens*, *Eleusine indica*, *Echlnochloa crus-galli*, *Poa annua*, *Cyperus esculentus* and *Alopecurus aequalis* and weeds such as *Siegesbeckia pubescens*, *Amaranthus lividus*, *Polygonum persicaria*, *Chenopodium album*, *Lamium amplexicaule*, *Acalypha australis*, *Galinsoga ciliata*, *Plantago asiatica*, *Portulaca oleracea*, *Commelina communis*, *Pinellia ternata* and *Artemisia princeps*, as well as improved control against perennial weeds such as *Eleocharis acicularis* and others.

While 3,5-dihalogenophenyl hydantoin compounds as
1,5-trimethylene-3-(3',5'-dichlorophenyl) hydantoin,
1,5-tetramethylene-3-(3',5'-dichlorophenyl) hydantoin,
1,5-trimethylene-3-(3',5'-dichlorophenyl)-2-thiohydantoin,
1,5-tetramethylene-3-(3',5'-dichlorophenyl)-2-thiohydantoin,
show a remarkably high antifungal activity against *Botrytis*, *Pellicularia* or *Chochlcobolus species*. This support the fact that these hydantoin derivatives are useful for the control of kidney bean gray mold disease, rice sheath blight disease and rice brown spot disease and others.

The active compound according to this invention may be formulated into a herbicide or fungicide by diluting it with an inert carrier or diluent which may be liquid or solid and, if desired, incorporating a surface active agent to obtain a herbicide or a fungicide in the form of a dust, emulsion, or wettable powder or as granules. If necessary, it is possible to add one or more other active ingredients, such as insecticide, nematocide, fertilizer, synergetic agent, another herbicide or fungicide or plant growth regulators.

Examples of liquid carriers which may be used include various solvents, for example, hydrocarbons such as kerosene, benzene and xylene; halogenated hydrocarbons such as chlorobenzene and dichloroethylene; lower alcohols such as ethanol, and ketones such as acetone. Examples of solid carrier are, bentonite, kaolin, clay, talc, activated clay, diatomaceous earth, siliceous sand and calcium carbonate.

Examples of surface active agents which may be used for formulating the herbicidal or fungicidal compositions according to this invention include alkylbenzene sulfonates, lignosulfonates, sulfate esters of higher alcohols or of polyoxyethylene aliphatic esters, polyoxyethylene sorbitan aliphatic esters, dialkyl sulfosuccinates and alkyltrimethyl ammonium chlorides.

The dosage rate of the compound according to this invention to be applied as active ingredient is not critical so far as intended herbicidal or fungicidal activity is achieved; however, it is preferable, in general, that 5 to 50 g of the compound is applied per 100 m^2, when it is used as herbicide.

It is proved from tests given hereinafter that the herbicide according to this invention shows by foliage or soil treatment excellent herbicidal activity against various weeds at germinating and growing stages.

Embodiments of formulations of herbicides and fungicides according to this invention are shown below; the number of the compound employed corresponds to the compound number in Tables 1 and 2 and "part" and "percentage" given therein are by weight unless otherwise defined.
(Emulsifiable oil).

Formulation Example 1.

A solution of 30 parts of compound No. 20 in a mixed solvent of 30 parts of N,N-dimethylformamide and 35 parts of xylene was mixed with 5 parts of polyoxy-

ethylene naphthylether sulfonate to give an emulsion containing 30% of the active ingredient.
(Wettable powder).

Formulation Example 2.

A wettable powder containing 50% of active ingredient was formulated by mixing and grinding 50 parts of compound No. 47, 10 parts of diatomaceous earth, 35 parts of kaolin and 5 parts of sodium dodecylbenzenesulfonate.
Granules.

Formulation Example 3.

A mixture of 5 parts of compound No. 19, 27 parts of diatomaceous earth, 66 parts of bentonite and 2 parts of Aerole CT—1, surface active agent available from Toho Chemical Industries Limited, was kneaded with water and granulated. The resulting granules were dried at 60°C for 2 hours to obtain a herbicide containing 5% of the active ingredient.

Following test Examples show herbicidal or fungicidal effect of the present invention.

Test Example 1.
(Paddy field application).

Wagner's pots (1/50 m^2) packed with soil from paddy field are employed

Soil containing seeds of barnyardgrass (*Echinochloa crus-galli*) and toothcup (*Rotala indica*) was spread on the surface area and rice seedlings (the three true leaf stage) were planted. While the depth of water was maintained at 3 cm, after 5 days herbicides according to this invention in the form of granule were uniformly applied to the surface of water in a dosage of 10 g and 30 g as active ingredient, per 100 m^2. Then, the water was drained from the bottom at a rate of a depth 3 cm/day for 3 days and 25 days after application herbicidal effect and phytotoxicity against rice plant were observed.

For the comparison purpose, similar tests were conducted using a commercially available herbicide comprising N,N-diethyl-S-(4-chlorobenzyl) thiolcarbamate, as a control chemical.

The results are given in Table 3.

The measures of the evaluation of herbicidal effect and phytotoxicity are as follows.

Figures	Herbicidal Effect	Phytotoxicity
0	None	None
1	Trace	Trace
2	Slight	Slight
3	Moderate	Moderate
4	Severe	Severe
5	Dead	Dead

TABLE 3

Compd. No.	Dosage g/100m²	Herbicidal effect		Phytotoxicity
		Barnyard-grass	Toothcup	
1	30	4	5	0
	10	3	3	0
3	30	4	5	0
	10	3	4	0
5	30	5	5	0
	10	4	5	0
6	30	5	5	0
	10	5	5	0
9	30	4	5	0
	10	3	4	0
12	30	4	4	0
	10	2	4	0
13	30	4	5	0
	10	3	4	0
15	30	5	5	0
	10	4	5	0
16	30	5	5	0
	10	5	5	0
17	30	5	5	0
	10	4	5	0
18	30	5	5	0
	10	5	5	0
19	30	5	5	0
	10	5	5	0
21	30	5	5	0
	10	5	5	0
23	30	5	5	0
	10	5	5	0
24	30	5	5	0
	10	4	5	0
25	30	5	5	0
	10	5	5	0
27	30	5	5	0
	10	5	5	0
30	30	4	5	0
	10	3	5	0

TABLE 3 (cont.)

Compd. No.	Dosage g/100m²	Herbicidal effect		Phytotoxicity
		Barnyard-grass	Toothcup	
31	30 10	5 4	5 5	0 0
33	30 10	5 5	5 5	0 0
36	30 10	5 5	5 5	0 0
37	30 10	5 5	5 5	0 0
38	30 10	4 3	5 4	0 0
40	30 10	5 5	5 5	0 0
42	30 10	5 4	5 5	0 0
43	30 10	5 4	5 5	0 0
45	30 10	5 5	5 5	0 0
46	30 10	5 5	5 5	0 0
48	30 10	5 5	5 5	0 0
51	30 10	5 4	5 5	0 0
52	30 10	5 5	5 5	0 0
54	30 10	5 5	5 5	0 0
55	30 10	4 3	5 5	0 0
Control	30 10	5 5	5 4	0 0
No Application		0	0	0

Test Example 2.
(Soil application).

Wheat, soybean and corn were seeded at a depth of 2—3 cm in 1/50 m^2 Wagner's pots containing seeds of crab-grass (*Digitaria adscendens*) and hairy galinsoga (*Galinsoga ciliata*) were spread on the surface area, then aqueous dilutions of wettable powders according to this invention were applied in a dosage per 100 m^2 of 10 g and 30 g to the surface area. After 25 days from the application, herbicidal effect and phytotoxicity were observed.

For the comparison purpose, the same tests were conducted using a commercially available herbicide comprising 3-(3',4'-dichlorophenyl)-1,1-dimethylurea as a control chemical.

The results are given in Table 4.

TABLE 4

Compd. No.	Dosage g/100m²	Herbicidal effect Crab-grass	Herbicidal effect Hairy galinsoga	Phytotoxicity Wheat	Phytotoxicity Soybean	Phytotoxicity Corn
2	30	4	5	0	0	0
	10	3	4	0	0	0
3	30	5	5	0	0	0
	10	4	5	0	0	0
4	30	5	5	0	0	0
	10	4	5	0	0	0
7	30	5	5	0	0	0
	10	5	5	0	0	0
8	30	5	5	0	0	0
	10	5	5	0	0	0
10	30	4	5	0	0	0
	10	3	4	0	0	0
12	30	4	4	0	0	0
	10	2	3	0	0	0
16	30	5	5	0	0	0
	10	5	5	0	0	0
22	30	5	5	0	0	0
	10	4	5	0	0	0
25	30	5	5	0	0	0
	10	5	5	0	0	0
26	30	5	5	0	0	0
	10	5	5	0	0	0
32	30	5	5	0	0	0
	10	5	5	0	0	0
34	30	5	5	0	0	0
	10	5	5	0	0	0
39	30	5	5	0	0	0
	10	3	5	0	0	0
41	30	4	5	0	0	0
	10	3	5	0	0	0
44	30	5	5	0	0	0
	10	5	5	0	0	0
46	30	5	5	0	0	0
	10	5	5	0	0	0
47	30	5	5	0	0	0
	10	5	5	0	0	0
50	30	5	5	0	0	0
	10	4	5	0	0	0

TABLE 4 (cont.)

Compd. No.	Dosage g/100m²	Herbicidal effect		Phytotoxicity		
		Crab-grass	Hairy galinsoga	Wheat	Soybean	Corn
52	30	5	5	0	0	0
	10	5	5	0	0	0
53	30	5	5	0	0	0
	10	4	5	0	0	0
Control	30	5	5	1	0	0
	10	4	5	0	0	0
No Application	—	0	0	0	0	0

Test Example 3.
(Foliar application).

Barnyardgrass (*Echinochloa crus-galli*), crab-grass (*Digitaria adscendens*) and radish (*Raphanus sativas*) were seeded in 1/50 m² Wagner's pots and after growing the plants emulsions containing 0.1% and 0.3% of active ingredients according to this invention were sprayed on the foliage in an amount of 10 l per 100 m² by a small pressurized spray-gun (0.5—1.0 kg/cm²).

After 20 days from the application, herbicidal effects were observed.

The times at which the herbicide was sprayed were 2—3 leaf stage in cases of barnyardgrass and crab-grass and first true leaf stage in case of radish.

For comparison, the same tests were conducted by a commercially available herbicide comprising 3,4-dichloropropionanilide as a control chemical.

The results are given in Table 5.

TABLE 5

Compd. No.	Concentration (%)	Herbicidal effect		
		Barnyard-grass	Crab-grass	Radish
6	0.3 0.1	5 4	5 5	5 5
8	0.3 0.1	5 4	5 5	5 3
11	0.3 0.1	5 4	5 5	5 4
12	0.3 0.1	4 3	5 4	4 3
14	0.3 0.1	5 4	5 5	5 4
20	0.3 0.1	5 5	5 5	5 5
21	0.3 0.1	5 5	5 5	5 5
23	0.3 0.1	5 4	5 5	5 4
25	0.3 0.1	5 5	5 5	5 5
33	0.3 0.1	5 5	5 5	5 5
35	0.3 0.1	5 4	5 5	5 5
41	0.3 0.1	4 2	4 3	4 3
46	0.3 0.1	5 4	5 5	5 4
49	0.3 0.1	5 4	5 5	5 5
50	0.3 0.1	5 4	5 5	5 5
52	0.3 0.1	5 4	5 4	5 3
53	0.3 0.1	4 3	5 4	5 3
Control	0.3 0.1	5 4	5 5	5 4
No Application	–	0	0	0

Test Example 4.

(Protection test against Kidney bean gray mold disease).

Kidney bean plants of true leaves stage were sprayed with 25 ml suspensions of the wettable powders of the tested compounds.

After drying, the leaves were inoculated with 6 mm agar disc containing pathogenic mycelia of *Botrytis cinerea*, and then the plants were incubated in the humidic chamber at 23°C for 4 days.

Protection value (%) was calculated according to the following equation.

$$\text{Protection value} = \frac{\text{(A)-Disease severity index treated}}{\text{Disease severity index untreated (A)}} \times 100$$

The results are shown in the table 6.

TABLE 6.

Compd. No.	Concentration (ppm)	Protection Value (%)
28	500	100
29	500	100
56	500	84.0
57	500	78.4
Untreated		0.0

Test Example 5.

(Preventive effect against Rice Sheath Blight Disease).

Rice plants (Cultivar; Kinmaze) of 5—6 leaf stage, grown on the 9 cm pots in the green house and cutted 20—30 cm high, were sprayed with suspensions (20 ml per pot) of wettable powders of the chemicals.

After drying, the plants were inoculated with pathogenic mycelia (*Pellicularia sasakii*), cultured for 7 days on the wheat bran medium.

These pots were covered with poly vinyl cases for holding humidity and incubated in the chamber (25—27°C). Twenty days after, disease severity index were examined and the preventive effects of the chemicals were calculated according to the following equation.

$$\text{Preventive Value} = \frac{\text{(A)-Disease severity index (treated)}}{\text{Disease severity index (untreated A)}} \times 100$$

The results are shown in the table 7.

TABLE 7.

Compd. No.	Concentration (ppm)	Preventive Value (%)
29	500	98.1
57	500	73.2
Untreated		0.0

Test Example 6.

(Preventive effect test of Rice brown spot disease).

Rice plants (cultivar; Kinmaze, 4—5 leaf stage), grown on the 9 cm pots in the greenhouse, were sprayed with suspensions (20 ml/pot) of wettable powder of the chemicals.

After drying, these plants were inoculated with the suspension containing pathogenic spores (*Chochliobolus miyabeanus*).

These plants were incubated in the humidic chamber (25—27°C).

After 48 hours, the number of lesions were counted and preventive value was calculated according to the following equation.

$$\text{Preventive value} = \frac{(\text{A}) - \text{number of lesions treated}}{\text{number of lesions untreated (A)}} \times 100$$

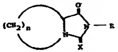
The results are shown in the table 8.

TABLE 8.

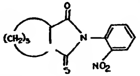
Compd. No.	Concentration (ppm)	Preventive Value (%)
28	500	91.8
29	500	85.9
56	500	98.6
Untreated		0.0

The specifically exemplified compounds are more readily absorbed and distributed in plants and therefore show increased herbicidal or fungicidal activity while at the same time giving less crop injury, phytotoxicity and environmental pollution. These compounds are readily broken down by microorganism in the soil and are not persistent in plants. The proline or pipecolinic acid moiety in an important feature in the hydantoins of the invention. Proline is well known as one of the essential amino acids, while pipecolinic acid has been found in plants such as apple and kidney bean and is also a metabolite of lysine in animals and plants.

No claim is made herein to any compound of the formula

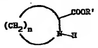


wherein X is sulphur, n is 3 or 4, R is a phenyl group substituted by one or more halogen atoms, lower alkyl groups, or lower alkoxy groups, or the compound



or to any method of making such compounds by reacting an imino acid of the formula

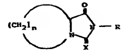
or an imino acid ester of the formula



in which R′ is a lower alkyl group and n is 3 or 4, with an aryl isothiocyanate of the formula R—NCS, wherein R is as defined above, or with ortho-nitrophenyl isothiocyanate.

SUBJECT TO THE FOREGOING DISCLAIMER.
WHAT WE CLAIM IS:—

1. A 1,5-Alkylene-3-substituted hydantoin having the general formula



Formula (I)

wherein n is 3 or 4, X is oxygen or sulphur and R is a phenyl group having at least one substituent which is a halogen atom, a lower alkyl group (as hereinbefore defined), a lower alkoxy group (as hereinbefore defined), a nitro group, a haloalkyl group or a halogenobenzyloxy group, or a naphthyl group, provided that when n is 4 and X is sulphur then R is not a monochlorophenyl group or a p-tolyl group.

2. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 1, in which n is 3, X is oxygen or sulphur and R is a phenyl group having at least one substituent which is a halogen atom, a lower alkyl group, a lower alkoxy group or a halogenobenzyloxy group.

3. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 1, in which n is 4, X is oxygen and R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group or halogenobenzyloxy group.

4. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 1, in which n is 4, X is sulphur and R is a phenyl group having at least one substituent which is a halogenobenzyloxy group.

5. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 4, in which R is a 4-(4′-chlorobenzyloxy) phenyl group.

6. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in any one of claims 1 to 3 in which R is a phenyl group having at least one halogen atom at the 4-position of the benzene ring.

7. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in any one of claims 1 to 3, in which R is a 3,5-dichlorophenyl group.

8. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 1 in which X is oxygen and R is a mono or disubstituted phenyl group, the substituents independently being a halogen atom, a lower alkyl group, a lower alkoxy group, a haloalkyl group, a nitro group or a halogenobenzyloxy group.

9. A 1,5-Alkylene-3-substituted hydantoin derivative as claimed in claim 1 in which X is sulphur, and R is phenyl having one or two substituents which are independently, haloalkyl, nitro or chlorobenzyloxy.

10. 1,5-Tetramethylene-3-(4′-chlorophenyl) hydantoin.

11. 1,5-Tetramethylene-3-(4′-bromophenyl) hydantoin.

12. 1,5-Tetramethylene-3-(3′-methyl-4′-chlorophenyl) hydantoin.

13. 1,5-Tetramethylene-3-(3′,4′-dichlorophenyl) hydantoin.

14. 1,5-Trimethylene-3-(4′-chlorophenyl) hydantoin.

15. 1,5-Trimethylene-3-(4′-bromophenyl) hydantoin.

16. 1,5-Tetramethylene-3-(4′-iodophenyl) hydantoin.

17. 1,5-Trimethylene-3-(3′,4′-dichlorophenyl) hydantoin.

18. 1,5-Tetramethylene-3[4′-(4″-chlorobenzyloxy) phenyl] hydantoin.

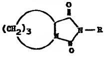
19. 1,5-Tetramethylene-3-(3′-methyl, 4′-bromophenyl) hydantoin.

20. 1,5-Tetramethylene-3-[4′-(4″-chlorobenzyloxy) phenyl]-2-thiohydantoin.

21. A 1,5-Alkylene-3-substituted hydantoin listed under any Compound Number in Table 1 or under any one of compound numbers 30, 35, 37, 42, 49, 54 and 55 in Table 2 other than those compounds claimed in any of claims 10 to 20.

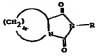
22. A herbicidal or fungicidal composition which comprises a carrier and as an active ingredient, a 1,5-alkylene-3-substituted hydantoin derivative as defined in claim 1.

23. A herbicidal or fungicidal composition as claimed in claim 22, in which the active ingredient is represented by the general formula



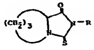
wherein R is as defined in claim 1.

24. A herbicidal or fungicidal composition as claimed in claim 22, in which the active ingredient has the general formula



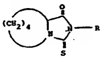
wherein R is as defined in claim 1.

25. A herbicidal or fungicidal composition as claimed in claim 22, in which the active ingredient has the general formula



wherein R is as defined in claim 1.

26. A herbicidal or fungicidal composition as claimed in claim 22, in which the active ingredient has the general formula



wherein R is as defined in claim 1.

27. A herbicidal composition as claimed in claim 22 in which R is phenyl substituted by nitro, halogen, lower alkyl, lower alkoxy, trifluoromethyl, or chlorobenzyloxy, or is naphthyl.

28. A herbicidal composition as claimed in any one of claims 23 to 26 in which R is a 4-halophenyl, 3-methyl-4-halophenyl, 4-(4'-halobenzyloxy) phenyl, or 3,4-dichlorophenyl group.

29. A herbicidal composition as claimed in claim 28 in which R is a 4-bromophenyl, 4-iodophenyl, 4-(4'-chlorobenzyloxy) phenyl, 3-methyl-4-chlorophenyl, 3-methyl-4-bromophenyl or 3,4-dichlorophenyl group.

30. A herbicidal composition as claimed in claim 25, in which the active ingredient is 1,5-tetramethylene-3-(4'-chlorophenyl) hydantoin.

31. A herbicidal composition as claimed in claim 29, in which the active ingredient is 1,5-tetramethylene-3-(4'-bromophenyl) hydantoin.

32. A herbicidal composition as claimed in claim 29, in which the active ingredient is 1,5-tetramethylene-3-(3'-methyl-4'-chlorophenyl) hydantoin.

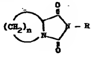
33. A herbicidal composition as claimed in claim 29, in which the active ingredient is 1,5-tetramethylene-3-(3',4'-dichlorophenyl) hydantoin.

34. A herbicidal or fungicidal composition which comprises a carrier and, as the active ingredient, a 1,5-alkylene-3-substituted hydantoin as claimed in claim 21.

35. A herbicidal or fungicidal composition substantially as described in any one of the Formulation Examples.

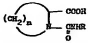
36. A fungicidal composition as claimed in claim 22, in which R is a 3,5-dichlorophenyl group.

37. A method for producing a 1,5-alkylene-3-substituted hydantoin derivative represented by the general formula



Formula II

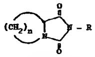
wherein n is 3 or 4, R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group, nitro group, haloalkyl group or halogenobenzyloxy group, which method comprises cyclizing an N-(N'-substituted carbamyl) imino acid represented by the general formula



Formula III

wherein n and R are as defined for Formula II.

38. A method for producing a 1,5-alkylene-3-substituted hydantoin derivative represented by the general formula



Formula II

wherein n is 3 or 4, R is a phenyl group having at least one substituent which is a halogen atom, lower alkyl group, lower alkoxy group, nitro group, haloalkyl group or halogenobenzyloxy group, which method comprises reacting an imino acid represented by the general formula

Formula IV

with an aryl isocyanate acid represented by the general formula

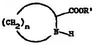
OCN—R

wherein R and n are as defined for Formula II.

39. A method for producing a 1,5-alkylene-3-substituted hydantoin derivative as claimed in claim 1, wherein x is sulphur, which method comprises reacting an imino acid represented by the general formula

Formula IV

or an imino acid ester of the general formula



Formula VI

wherein R' is a lower alkyl grouip and n is 3 or 4 with an aryl isothiocyanate represented by the general formula

SCN—R

wherein R is as defined for Formula I above.

40. A method of preparing a 1,5-alkylene-3-substituted hydantoin substantially as described in any one of the Preparative Examples.

41. A method of killing plants or of controlling or preventing the growth of plants which method comprises applying a compound as claimed in any one of claims 1 to 20 or a herbicidal composition as claimed in any one of claims 22 to 35 to susceptible plants or an area in which their growth is to be prevented.

42. A method of killing plants as claimed in claim 41 substantially as described in any one of test examples 1 to 3.

43. A method of killing fungus or of preventing or controlling the growth of

fungus which method comprises applying a compound as claimed in any one of claims 1 to 21 or a fungicidal composition as claimed in any one of claims 22 to 26 or 34 to 36 to a susceptible fungus or an area in which the growth of fungus is to be prevented.

44. A method of preventing fungal growth as claimed in claim 43 substantially as described in any one of test examples 4 to 6.

45. A method as claimed in claim 41 or claim 42 wherein the active compound is applied at a rate of from 5 to 50 g/100 m^2.

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